PATENT SPECIFICATION

839,407

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COMPLETE SPECIFICATION

NO DRAWINGS

Detergent Compositions

We, BRITISH NYLON SPINNERS LIMITED, of Pontypool, Monmouthshire, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to detergent composition for textiles, notably for those textiles consisting of synthetic linear polymers, and in particular to such detergent compositions which also exercise an antistatic effect.

It is well known that synthetic linear polymer textile material, e.g. polyamide textile material, is liable to become electrostatically charged as a result of adventitious friction in the course of use, for example, friction arising from movements on the part of the wearer of the textile material concerned. There is, moreover, evidence to the effect that the soiling during wear of for instance, a nylon shirt (nylon being polyhexamethylene adipamide) may be due in considerable measure to the electrostatic attraction of particles of dirt. Efforts have accordingly been made to devise anti-static agents capable of hindering the accumulation of such electric charges. These anti-static agents, though they may be effective when applied, are, however, frequently insufficiently resistant to rinsing.

The ingredient of the present detergents responsible (or mainly responsible) for their detergency is an anionic surface active agent, i.e. a water-soluble compound, having lipophilic and hydrophilic groups in the anion (cf. pages 108 and 109 of "Surface Active Agents" by C. B. F Young and K. W. Coons, 1945, Chemical Publishing Co. Inc.), a genus which includes, inter alia, the alkali soaps, e.g. sodium stearate (a constituent of common soap), alkali metal fatty alcohol sulphates, e.g. sodium cetyl sulphate, alkylaryl sulphonates, e.g. sodium p-dodecylbenzene sulphonate and alkyl ethers of glyceryl mono-phosphate or sulphate e.g. the disodium Salt of the dodecyl octyl diether of glyceryl mono-phosphate.

The present detergent compositions also contain a conventional water-soluble inorganis salt of neutral or alkaline reaction, e.g. sodium carbonate, sodium sulphate, sodium borate. Now it has been found that by incorporating a minor proportion of a cationic surface active agent, that is, a water-soluble compound having lipophilic and hydrophilic groups in the cation (loc. cit.), such as trimethyl-octadecyl-ammonium chloride, an anti-static effect may be imparted. Normally anionic and cationic surface active agents undergo mutual precipitation when mixed in solution. Surprisingly, however, experiments have shown, that provided the cationic agent is first mixed with sufficient of an inorganic salt powder, before the incorporation of the anionic agent, the aforesaid precipitation can be avoided. It is preferred that the cationic agent be applied in the form of a solution, to a sufficiency of solid inorganic salt, so as to coat the individual crystals or granules thereof without making the powder, as a whole, wet. Mixtures so obtained can be safely mixed with the desired anionic surface active agent without fear of precipitation occurring when the resulting detergent mixture is dissolved in water for use in washing. Morever, the anti-static effect produced by the employment of the present detergent compositions withstands rinsing and tends even to increase during the course of successive washings. The present detergent compositions also appear to have the advantage of hindering re-deposition of the dirt on the fabric

Price

whilst it is in the wash liquor. Although the numerical data quoted in the following Examples only relate to the electrostatic charges, extensive trials involving the wearing and washing of garments, wherein the present detergent compositions are compared with similar detergent compositions devoid of the cationic agents, show the superiority of the former.

Accordingly the present invention relates to a process for making detergent compositions comprising mixing an alcoholic, aqueous or aqueous-alcoholic solution of a cationic surface active agent, which is a quaternary ammonium (including morpholinium and pyridinium), or phosphonium salt, with a sufficient quantity of a powdered water-soluble alkaline-reacting or neutral-reacting inorganic salt, so that the weight of said salt remaining undissolved is not less than the weight of the cationic surface active agent, drying if necessary to remove any visible liquid, and then intimately mixing with a quantity of an anionic surface active agent weighing from 2 to 1000 times the weight of the cationic surface active agent employed.

When drying is effected in order to remove any visible liquid, the dried product is advantageously powered so as to facilitate the subsequent mixing with the anionic surface active agent. It is however preferred that the quantity of the solution of the cationic surface active agent employed should only suffice to coat the individual crystals or granules of the inorganic salt powder, without making the latter visibily wet. In this case there is thus no visible liquid present and therefore no drying is required. The anionic surface active agent may be introduced either as the pure compound or, for example, in the form of an aqueous solution or paste, or otherwise conveniently diluted.

An anti-static effect is produced even when the proportion of cationic surface active agent to anionic surface active agent is as low as 1-500 or even 1-1000. However it is preferred that the weight of the anionic agent be from 10 to 200 times the weight of the cationic agent.

The cationic surface active agent may be for example:—

octadecyl-trimethylammonium chloride
octadecenyl-trimethylammonium chloride
octadecadienyl-trimethylammonium chloride
dodecyl-trimethylammonium chloride
hexadecyl-trimethylammonium chloride
didodecyl-dimethylammonium bromide
dioctadecyl-dimethylammonium chloride
benzyl tri-(dimethylamino) phosphonium chloride
benzyl-stearyl-dimethylammonium chloride
hexadecyl methyl morpholinium methosulphate
hexadecyl pyridinium chloride
dodecyl pyridinium chloride

Those cationic surface active agents are preferred which are capable of imparting strong antistatice effect when applied to the textile material by themselves.

Examples of the inorganic salt to be employed are:—

anhydrous sodium carbonate
sodium carbonate decahydrate
sodium bicarbonate
sodium borate
sodium sulphate
trisodium orthophospate
sodium metaphosphate
sodium pyrophosphate
disodium hydrogen phosphate
sodium tripolyphosphate
sodium perborate

The anionic surface active agent may be for example:—

sodium cetyl sulphate
sodium oleyl sulphate
sodium dodecyl sulphate
sodium p-dodecylbenzene sulphonate
triethanolammonium p-dodecylbenzene sulphonate
sodium stearate
sodium oleate
sodium isopropyl naphthalene sulphonate
oleoyl methyl taurine
sodium dioctyl monosulphosuccinate

Mixtures of such inorganic salts, as above may be used. Other conventional ingredients may optionally be included in the present detergents, such as, for instance, china clay, sodium silicate, magnesium silicate.

The following Examples, in which the parts are by weight are intended to illustrate, but not limit the present invention.

Example I

9.85 Parts of a 75% solution of dioctadecyl-dimethylammonium chloride in isopropanol are diluted with 6 parts of methanol and thoroughly mixed with 12 parts of anhydrous sodium carbonate powder. The resulting powder is then mixed with 50 parts of common soap powder.

A plain weave fabric of 30 denier nylon yarn (10 filaments) is washed repeatedly and examined as to its tendency to become electrostatically charged in the following manner:—

The fabric, divided into 11 strips, is immersed and agitated for 3 minutes, in 100 times its own weight of a 0.1% aqueous solution of the above detergent composition at 60°C. The fabric strips are then removed, rinsed once with warm water and twice with cold water, and dried. One strip is set aside and the remaining ten washed again, rinsed and dried as before. Another strip is set aside and the process repeated

until the final strip has received 11 washes.

The strips of fabric are stored for 24 hours in an atmosphere of 65% Relative Humidity at 70°F. together with 10 strips of the same fabric which have not been washed. Each strip measuring 3" x 2" is then tested as follows. The fabric placed on filter paper is brushed 3 times with a nylon brush and put into the inner container of a Faraday Ice Pail. The charge produced, is a circuit of constant capacity, is read in terms of voltage from a Rothschild Electrostatic Voltmeter (obtainable from Messrs. Rothschild of Waffenplatz, Zurich), the following results being obtained:—

No. of washes	1	2	3	4	5	6	7	8	9	10	11
Volts (negative)	45	200	200	250	30	100	20	30	60	60	45

Unwashed fabric (mean of 10 tests):— 300 volts.

Example 2

18 parts of 50% solution of octadecenyltrimethylammonium chloride are diluted with 18 parts of methanol and mixed with 98 parts of sodium perborate and 350 parts of sodium tripoly-phosphate. The resulting powder is then compounded with 880 parts of a 75% aqueous paste of sodium p-dodecyl benzene sulphonate. A detergent composition in powder form is obtained on drying.

A plain weave nylon fabric is washed with the above detergent composition and tested in the way described in Example 1. The following results being obtained:—

No. of washes	1	2	3	4	5	6	7	8	9	10	11
Volts (negative)	250	330	350	230	150	80	200	25	0	0	0

Unwashed fabric (mean of 10 tests):— 420 volts.

Example 3

The cationic agent employed is a mixture of equal parts of octadecadienyltrimethylammonium chloride and octadecenyltrimethyl-ammonium chloride. This mixture is dissolved in its own weight of isopropyl alcohol so as to produce a 50% solution.

20 Parts of the above 50% solution are diluted with 20 parts of methanol and mixed with 30 parts of powdered sodium perborate and 50 parts of powdered anhydrous sodium carbonate. A powder, which is not visibly wet, results. This powder is then intimately mixed with the following salts:—

20 parts of sodium p-dodecyl benzene sulphonate
40 parts of sodium tripolyphosphate
40 parts of sodium sulphate

The resultant mixture constitutes the detergent composition; the ratio by weight of anionic to cationic agent contained therein is 2:1.

Strips of nylon fabric are washed with 100 times their weight of a 0.1% aqueous solution of the above detergent composition at 60°C. and the electrostatic charge produced measured as described in Example 1. It is found that the charge is only about 15% of that generated on the unwashed fabric.

Example 4

Example 3 is repeated except that only 2 parts of the 50% solution of cationic agent are taken. The electrostatic charge is 30% of that found on the unwashed fabric.

Even when only 0.2 part of the 50% solution of cationic agent is employed, the electrostatic charge is much less than that produced on the unwashed fabric.

Similar results are obtained when the fabric is made of cellulose acetate, cellulose triacetate or polyethylene terephthalate, instead of nylon.

British Patent No. 753,848 claims, inter alia, a washing and cleansing agent, containing a water-soluble salt of a sulphuric acid ester of a water-insoluble or water-dispersible alkylbenzene-N-hydroxyalkyl-sulphamide of general formula:—

R-para-phenylene-SO_2NH-R'OH in which R donates a higher molecular weight alkyl residue having at least six carbon atoms and R' denotes an aliphatic hydrocarbon residue having at least two carbon atoms, which residue may also contain an additional hydroxyl group or groups and may be interrupted by one or more oxygen atoms, which agent contains at least one additional surface-active agent and/or washing agent.

British Patent No. 759,837 claims a soap-free composition for the cleansing of the human body or for toilet purposes, containing a major proportion of a neutral-reacting acid-stable, anion-active compound and a minor proportion of a complex obtained by reaction between an acid-stable, anion-active compound and a cation-active substance

WHAT WE CLAIM IS:—

1. Process for the manufacture of detergent compositions comprising mixing an alcoholic, aqueous or aqueous-alcoholic solution of a cationic surface active agent, which is a quaternary ammonium, (including morpholinium and pyridinium) or phosphonium salt, with a sufficient quantity of a powdered water-soluble alkaline-reacting or neutral-reacting inorganic salt, so that the weight of said salt remaining undissolved is not less than the weight of the cationic surface active agent, drying if necessary to remove any visible liquid, and then intimately mixing with a quantity of an anionic surface active agent weighing from 2 to 1000 times the weight of the cationic surface agent employed.

2 Process for the manufacture of detergent compositions as claimed in Claim 1, wherein the quantity of the solution of the cation surface active agent only suffices to coat the individual crystals or granules of the inorganic salt powder, without making the latter visibly wet, so that no drying is required.

3. Process for the manufacture of detergent compositions as claimed in Claim 1 or 2 wherein the weight of anionic surface active agent is from 10 to 200 times the weight of the cationic agent.

4. Process for the manufacture of detergent compositions as claimed in any of the preceding Claims, wherein the cationic surface active agent comprises a mixture of octadecadienyltrimethylammonium chloride and octadecenyltrimethylammonium chloride.

5. Process for the manufacture of detergents compositions substantially as described with reference to the foregoing Examples.

6. Detergent compositions whenever manufactured according to a process claimed in any of the foregoing Claims.

S. CLARK,
Chartered Patent Agent.

PROVISIONAL SPECIFICATION

Detergent Compositions

We, BRITISH NYLON SPINNERS LIMITED, of Pontypool, Monmouthshire, a British Company, do hereby declare this invention to be described in the following statement:

This invention relates to detergents for textiles consisting of synthetic linear polymers, and in particular to such detergents which also exercise an antistatic effect.

It is well known that synthetic linear polymer textile material, e.g. polyamide textile material, is liable to become electrostatically charged as a result of adventitious friction in the course of use, for example, friction arising from movements on part of the wearer of the textile material concerned. There is, moreover, evidence to the effect that the soiling during wear of for instance, a nylon shirt (nylon being polyhexamethylene adipamide) may be due in considerable measure to the electrostatic attraction of particles of dirt. Efforts have accordingly been made to devise anti-static agents capable of hindering the accumulation of such electric charges. These anti-static agents, though they may be effective when applied, are, however, frequently insufficiently resistant to rinsing.

The ingredient of the present detergents responsible (or mainly responsible) for their detergency is an anionic surface active agent, i.e. a water-soluble compound, having lipophilic and hydrophilic groups in the anion (cf. pages 108 and 109 of "Surface Active Agents" by C. B. F Young and K. W. Coons, 1945, Chemical Publishing Co. Inc.), a genus which includes, inter alia, the alkali soaps e.g. sodium stearate (a constituent of common soap), alkali metal fatty alcohol sulphates, e.g. sodium cetyl sulphate, alkylaryl sulphonates, e.g. sodium p-dodecylbenzene sulphonate and alkyl monoglyceryl phosphates or sulphates e.g. lauryl octyl monoglyceryl phosphate.

The present detergents also contain a conventional water-soluble inorganic salt of neutral or alkaline reaction, e.g. sodium carbonate, sodium sulphate, sodium borate. Now it has been found that by incorporating a minor proportion of a cationic surface active agent, that is, a water-soluble compound having lipophilic and hydrophilic groups in the cation (loc. cit.), such as trimethyl-octadecyl-ammonium chloride, an anti-static effect may be imparted. Normally anionic and cationic surface active agents undergo mutual precipitation when mixed in solution. Surprisingly, however, experiments have shown, that provided the cationic agent is first applied to the solid inorganic salt in the form of a solution, mixed with a sufficiency of said salt so as to coat the individual crystals or granules thereof without making the powder, as a whole, wet, then the mixture so obtained can be safely mixed with the desired anionic surface active agent without fear of precipitation occurring when the resulting detergent mixture is dissolved in water for use in washing. Moreover, the anti-static effect produced by the employment of the present detergents withstands rinsing and tends to increase during the course of successive washings.

Accordingly the present invention relates to a process for making detergents comprising applying an alcoholic, aqueous or aqueous-alcoholic solution of a cationic surface active agent which is quaternary ammonium, phosphonium, or morpholinium salt, wherein the nitrogen atom bears, inter alia, a long chain hydrocarbon residue group, to at least 10 times its weight of a powdered water-soluble alkaline—or neutral-reacting inorganic salt, and mixing well so that said solution coats the individual crystals or granules of the salt without making the powder, as a whole, wet, and then mixing the resulting powder with a quantity of an anionic surface active agent weighing 10-1,000 times the weight of the cationic active agent employed.

The cationic surface active agent may be

for example:—
octadecyl-trimethylammonium chloride
octadecenyl-trimethylammonium chloride
octadecadienyl-trimethylammonium chloride
dodecyl-trimethylammonium chloride
didodecyl-dimethylammonium bromide
dioctadecyl-dimethylammonium chloride
benzyl tri-(dimethylamino) phosphonium chloride
cetyl methyl morpholinium methosulphate

Those cationic surface active agents are preferred which are capable of imparting an antistatic effect when applied to the textile material by themselves.

Examples of the inorganic salt to be employed are:—
anhydrous sodium carbonate
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sodium bicarbonate
sodium borate
sodium sulphate
trisodium orthophospate
sodium metaphosphate
sodium pyrophosphate
disodium hydrogen phosphate
sodium perborate

The anionic surface active agent may be for example:—
sodium cetyl sulphate
sodium dodecyl sulphate
sodium p-dodecylbenzene sulphate
sodium stearate
sodium oleate
sodium isopropyl naphthalene sulphonate
oleyl methyl taurine
sodium dioctyl monosulphosuccinate
sodium tripolyphosphate

Mixtures of such inorganic salts, as above may be used. Other conventional ingredients may optionally be included in the present detergents, such as, for instance, china clay, sodium silicate, magnesium silicate.

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No. of washes	1	2	3	4	5	6	7	8	9	10	11
Volts (negative)	45	200	200	250	30	100	20	30	60	60	45

Unwashed fabric (mean of 10 tests):—300 volts.

Example 2

18 parts of 50% solution of octadecenyl-trimethylammonium chloride are diluted with 18 parts of methanol and mixed with 98 parts of sodium perborate and 350 parts of sodium tripoly-phosphate. The resulting powder is then compounded with 880 parts of a 75% aqueous paste of sodium p-dodecyl benzene sulphonate. A detergent powder is obtained on drying.

A plain weave nylon fabric is washed with the above detergent and tested in the way described in Example 1. The following results being obtained:—

No. of washes	1	2	3	4	5	6	7	8	9	10	11
Volts (negative)	250	330	350	230	150	80	200	25	0	0	0

Unwashed fabric (mean of 10 tests):—420 volts.

S. CLARK,
Chartered Patent Agent.

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